Supporting Information

Synthesis and Structural Characterization of Three Unique *Helicobacter pylori* α-Cholesteryl Phosphatidyl Glucosides

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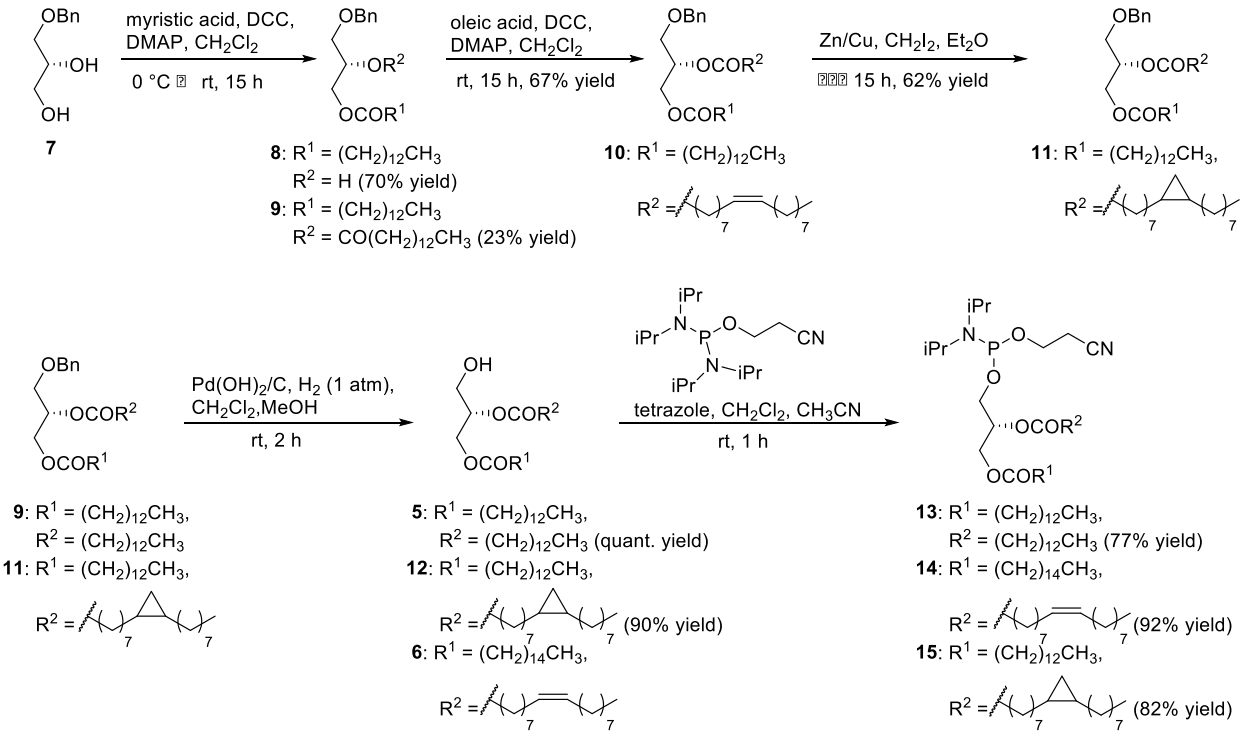
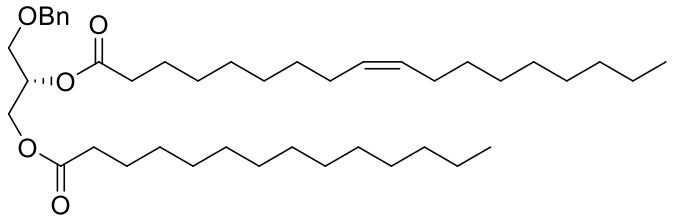
General Experimental

All reactions were conducted under a dry argon atmosphere. Solvents including tetrahydrofuran (THF) 99.9%, chloroform ($CHCl_3$) 99.9%, pyridine (pyr) 99.0%, acetone 99.8%, dichloromethane (CH_2Cl_2) 99.9%, and methanol 99.8% were purchased as anhydrous in a sure seal bottle under argon atmosphere. To insure that solvents were extra dry, they were subjected to activated molecular sieves. Trimethylsilyl iodide (TMSI) was stored at -15 °C in a sealed jar of drierite. Cholesterol (95%) and tetrabutylammonium iodide (TBAI) were stored at 80 °C under vacuum for at least 48 h prior to use. All other chemical reagents were commercial grade and used without further purification. Glass-backed TLC plates (Silica Gel 60 with a 254 nm fluorescent indicator) were used without further manipulation and stored over desiccant. Developed TLC plates were visualized with ammonium molybdate/cerium (IV) sulfate stain and heat provided by a hotplate. Silica gel flash column chromatography was performed using flash silica gel (32-63 μm) and employed a solvent polarity correlated with TLC mobility. NMR spectra were obtained using a 500 and 600 spectrometers and are reported in parts per million (δ) relative to chloroform (^{1}H NMR δ = 7.26, ^{13}C NMR δ = 77.16) or methanol (^{1}H NMR δ = 3.31, ^{13}C NMR δ = 49.0). ^{31}P NMR was taken on a 300 MHz (120 MHz) and an AV-500 (200 MHz). Coupling constants (*J*), of proximal nuclei were averaged to match. High resonance mass spectrometry samples were analyzed either by electrospray ionization mass spectrometry in positive mode using flow-injection analysis. Optical rotations were measured at 598 nm using a commercial polarimeter, in a 100 mm cell or 10 mm cell.



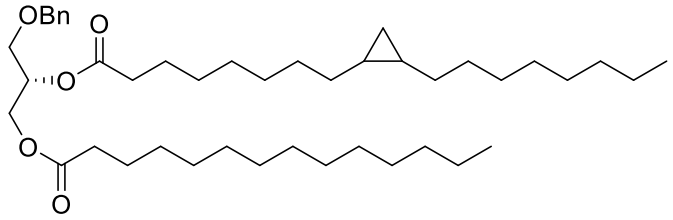
1-(Tetradecanoyl)-3-*O*-benzyl-*sn*-glycerol (8) and 1,2-(tetradecanoyl)-3-*O*-benzyl *sn*-glycerol (9): Diol **7**[1] (2.88 g, 15.8 mmol) was azeoptropically dried with benzene (3 x 4 mL) and placed under high vacuum overnight. Myristic acid (4.33 g, 18.9 mmol) and DMAP (0.20 g, 1.60 mmol) was added to **7** and then dissolved with dry CH_2Cl_2 (12 mL) under argon. A solution of DCC (4.89 g, 23.7 mmol) in dry CH_2Cl_2 (8 mL) was transferred to the reaction vessel containing **7** via cannula over 20 min at 0 ºC. The reaction was allowed warm to rt and stirred overnight. The white suspension was diluted with CH_2Cl_2 (~20 mL) and filtered over a pad of celite. After concentrating the filtrate, the crude oil was purified by gradient flash column chromatography (5 →30% EtOAc:hexanes) to afford **8**[1] (4.37 g, 70% yield) and **9**[1] (2.18 g, 23% yield. Characterization for compound **8**: $[\alpha]_D^{25}$ +2.67 (*c* 0.006, $CHCl_3$); R_f = 0.35 (4:1 hexanes:EtOAc); ^{1}H NMR (600 MHz, C_6D_6): δ 7.21 - 7.09 (m, Ph, 5H), 4.29 (s, O-CH_2, 2H), 4.18 (d, *J* = 5.5 Hz, *sn*-1-CH_2, 2H), 3.97-3.95 (m, *sn*-2-CH, 1H), 3.34 (dd, *J* = 5.8, 4.8 Hz, *sn*-3-

CH_2, 2H), 3.19 (d, *J* = 4.8 Hz, *sn*-2-OH, 1H), 2.15 (t, *J* = 7.7 Hz, CO-CH_2, 2H), 1.56 – 1.54 (m, 2H), 1.30 – 1.19 (m, 20H), 0.90 (t, *J* = 7.3 Hz, CH_3, 3H); ^{13}C NMR (150 MHz, C_6D_6): δ 173.4 (C=O), 138.6, 128.6, 127.9, 127.8, 73.5, 71.6, 69.1, 65.8, 34.3, 32.4, 30.2, 30.2, 30.1, 30.0, 29.6, 29.8, 29.5, 25.3, 23.1, 14.4; HRMS (ESI-Ion Trap) *m/z*: $[M+Na]^+$ calcd for $C_{24}H_{40}O_4Na$, 415.2819; found . Characterization for compound **9**[1]: R_f = 0.74 (4:1 hexanes:EtOAc).



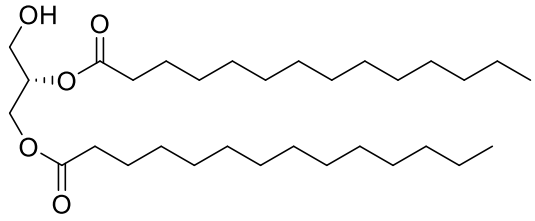
1-(Tetradecanoyl)-2-(9Z-octadecanoyl)-3-*O*-benzyl *sn*-glycerol (10): A solution of DCC (2.62 g, 12.7 mmol) was added dropwise via a cannula to a solution of compound **8** (3.32 g, 8.46 mmol), DMAP (0.10 g, 0.85 mmol), and oleic acid (2.87 g, 10.1 mmol) over 25 min at room temperature. The suspension was stirred for 20 h at rt and then filtered through celite. The celite was washed with CH_2Cl_2 and the filtrate was concentrated to a crude product that was purified by gradient flash column chromatography (5→10% EtOAc:hexanes) to afford **10** (3.72 g, 67% yield) as a clear oil: $[\alpha]_D^{25}$ +1.56 (*c* 0.012, $CHCl_3$); R_f = 0.70 (4:1 hexanes/EtOAc 9:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.24 7.17 (m, Ph, 5H), 5.27-5.25 (m , HC=CH, 2H), 5.17 – 5.15 (m, *sn*-2-CH, 1H), 4.47 (d, *J* = 11.9 Hz, O-CH_2, 1H), 4.43 (d, *J* = 11.9 Hz, O-CH_2, 1H), 4.27 (dd, *J* = 11.9, 3.8 Hz, *sn*-1-Cha, 1H), 4.11 (dd, *J* = 11.8, 6.4 Hz, *sn*-1-CHb, 1H), 3.50 (dd, *J* = 5.2, 2.1 Hz, *sn*-3-CH_2, 2H), 2.23 (t, *J* = 7.5 Hz, CO-CH_2, 2H), 2.19 (t, *J* = 7.5 Hz, CO-CH_2, 2H), 1.93 (dt, *J* = 13.4, 6.6 Hz, 4H), 1.52 (m, 4H), 1.25 – 1.17 (m, 40H), 0.80 (t, *J* = 7.1 Hz, 2xCH_3, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 173.3, 173.0, 137.8, 130.0, 129.7, 128.4, 127.8, 127.7, 73.3, 70.1, 68.3, 62.7, 34.3, 34.2, 32.0, 32.0, 29.8, 29.8, 29.8, 29.7, 29.7, 29.6, 29.5, 29.4, 29.4, 29.3, 29.3, 29.2, 29.2,

29.1, 27.3, 27.2, 25.0, 24.9, 22.8, 22.7, 14.2; HRMS (ESI-Ion Trap) *m/z*: $[M+NH_4]^+$ calcd for $C_{42}H_{76}NO_5^+$, 674.5718; found 674.5730.

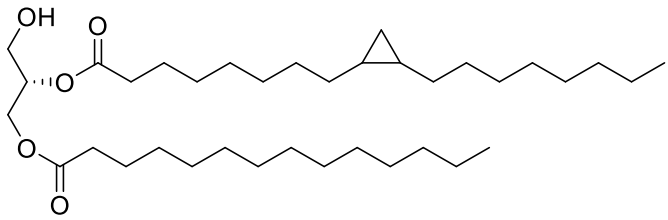


1-(Tetradecanoyl)-2-(9-cyclopropyl-nonadecanoyl)-3-*O*-benzyl *sn*-glycerol (11): Compound **10** (3.70 g, 6.00 mmol), Zn/Cu (1.67 g, 13.0 mmol), and CH_2I_2 (1.81 mL, 23.0 mmol) were suspended with Et_2O (30 mL). The suspension was then refluxed (40 ºC) for 15 h. Water (30 mL) was added and then the suspension was filtered through a pad of celite. The filtrate was extracted with Et_2O and then the organic layer was washed with aqueous NH_4Cl and sat. $NaHCO_3$. After drying over $MgSO_4$, the crude was concentrated and purified by gradient flash column chromatography (0 →8% EtOAc:hexanes) to afford **11** as a clear oil (2.35 g, 62% yield): $[\alpha]_D^{25}$ +4.43 (*c* 0.010, $CHCl_3$); R_f = 0.38 (9:1 hexanes:EtOAc); ^1H NMR (800 MHz, $CDCl_3$): δ 7.30 – 7.21 (m, Ph, 5H), 5.21 – 5.19 (m, *sn*-2-CH, 1H), 4.51 (d, *J* = 12.2 Hz, O-CH_{2a}, 1H), 4.47 (d, *J* = 12.2 Hz, O-CH_{2b}, 1H), 4.31 (dd, *J* = 11.8, 3.8 Hz, *sn*-1-CHa, 1H), 4.15 (dd, *J* = 11.8, 6.4 Hz, *sn*-1-CHb, 1H), 3.54 (dd, *J* = 5.1, 2.1 Hz, *sn*-3-CH_2, 2H), 2.27 (t, *J* = 7.5 Hz, CO-CH_2, 2H), 2.23 (t, *J* = 7.5 Hz, CO-CH_2, 2H), 1.58 – 1.52 (m, 4H), 1.33 – 1.08 (m, 48H), 0.83 (t, *J* = 6.7 Hz, CH_3, 6H), 0.63 – 0.56 (m, cyclopropyl 2xCH, 2H), 0.52 (ddd, *J* = 9.7, 4.16, 4.10 Hz, cyclopropyl CH_{2a}, 1H), -0.38 (app. q, *J* = 9.7, 5.3, 4.16 Hz, cyclopropyl CH_{2b}, 1H); ^{13}C NMR (200 MHz, $CDCl_3$): δ 173.3, 173.0, 137.8, 128.4, 127.8, 127.7, 73.3 (O-CH_2), 70.0 (*sn*-2-CH), 68.3 (*sn*-3-CH_2), 62.7 (*sn*-1-CH_2), 34.4, 34.1, 32.0, 30.3, 30.2, 29.8, 29.8, 29.7, 29.7, 29.6, 29.5, 29.4, 29.4, 29.4, 29.3, 29.2, 29.1, 28.8, 28.7, 25.0, 24.9, 22.8, 22.7, 15.8, 15.7, 14.2, 11.0 (cyclopropyl CH_2); HRMS (ESI-Ion Trap) *m/z*: $[M+NH_4]^+$ calcd for $C_{43}H_{78}NO_5^+$, 688.5875; found 688.5874.

General protocol for debenzylation: Diacyl-*O*-benzyl glycerol (**9** and **11**) and $Pd(OH)_2/C$ (10% wt. of diacylglycerol) were suspended with CH_2Cl_2:MeOH (~10 mL). Then H_2 (g) 1 atm was bubbled into the suspension for 30 min. After stirring at rt for 2 h, the suspension was filtered through a pad of celite. The filtrate was then concentrated and purified by gradient flash column chromatography (5 →20% EtOAc:hexanes) to afford a clear oil.



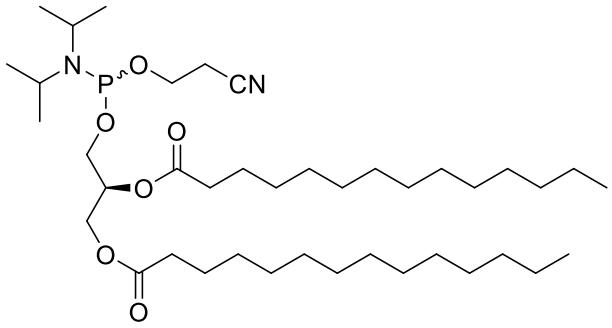
1,2-(Tetradecanoyl)-*sn*-glycerol (5)[1]: Compound **9** (1.00 g, 1.65 mmol) was debenzylated and purified to afford **5** (0.85 g, quant. yield) as a clear oil: R_f = 0.28 (4:1 hexanes:EtOAc); ^{1}H NMR (800 MHz, $CDCl_3$): δ 5.08 (app. quin, *J* = 5.1, 5.1, 5.1, 5.0 Hz, *sn*-2-CH, 1H), 4.32 (dd, *J* = 11.9, 4.5 Hz, *sn*-1-CHa, 1H), 4.24 (dd, *J* = 11.9, 5.7 Hz, *sn*-1-CHb, 1H), 3.73 (app. d, *J* = 3.1 Hz, *sn*-3-CH_2, 2H), 2.34 (t, *J* = 7.6 Hz, CO-CH_2, 2H), 2.32 (t, *J* = 7.6 Hz, CO-CH_2, 2H), 2.04 (br. s, *sn*-3-OH, 1H), 1.63 – 1.58 (m, 4H), 1.30 – 1.25 (m, 40H), 0.88 (t, *J* = 7.1 Hz, CH_3, 3H); ^{13}C NMR (200 MHz, $CDCl_3$): δ 174.0, 173.6, 72.2 (*sn*-2-CH), 62.1 (*sn*-1-CH_2), 61.7 (*sn*-3-CH_2), 34.4, 34.3, 32.1, 29.8, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 25.1, 25.0, 22.8, 14.3.



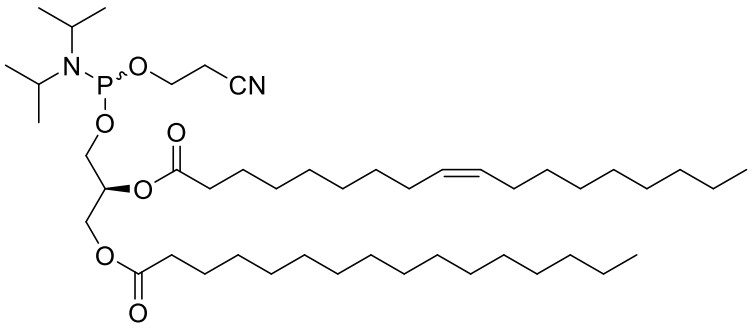
1-(Tetradecanoyl)-2-(9-cyclopropyl-nonadecanoyl)-*sn*-glycerol (12): Compound **11** (0.40 g, 0.60 mmol) was debenzylated and purified to afford **12** (0.32 g, 90% yield) as a clear oil: $[\alpha]_D^{25}$ -

1.67 (*c* 0.002, $CHCl_3$); R_f = 0.36 (4:1 hexanes:EtOAc); ^{1}H NMR (600 MHz, C_6D_6): δ 5.19 – 5.16 (m, *sn*-2-CH, 1H), 4.36 (dd, *J* = 12.0, 3.8 Hz, *sn*-1-CH_a, 1H), 4.17 (dd, *J* = 12.0, 6.2 Hz, *sn*-1-CH_b, 1H), 3.51 (d, *J* = 3.7 Hz, *sn*-3-CH_2, 2H), 2.19 (t, *J* = 7.9 Hz, CO-CH_2, 2H), 2.15 (t, *J* = 7.9 Hz, CO-CH_2, 2H), 1.60-1.55 (m, 4H), 1.47 – 1.40 (m, 5H), 1.37 – 1.18 (m, 40H), 0.91 (t, *J* = 6.0 Hz, CH_3, 6H), 0.71 – 0.68 (m, cyclopropyl CH, 2H), 0.67 – 0.65 (m, cyclopropyl CH_{2a}, 1H), -0.24 (app. q, *J* = 4.9, 4.8, 4.2 Hz, cyclopropyl CH_{2b}; ^{13}C NMR (150 MHz, C_6D_6): δ 173.2, 173.1, 72.6 (*sn*-2-CH), 62.7 (*sn*-1-CH_2), 61.5 (*sn*-3-CH_2), 34.5, 34.2, 32.4, 30.8, 30.7, 30.2, 30.2, 30.2, 30.1, 30.0, 30.0, 29.9, 29.8, 29.7, 29.5, 29.3, 29.2, 25.3, 25.2, 23.2, 16.3 (cyclopropyl CH), 16.2 (cyclopropyl CH), 14.4, 11.5 (cyclopropyl CH_2); HRMS (ESI-Ion Trap) *m/z*: $[M+H]^+$ calcd for $C_{36}H_{69}O_5^+$, 581.5140; found 581.5130.

General protocol for the synthesis of diacylglycerol phosphoramidite (13-15): The diacylglyerol (**5-6,12**) was azeotropically dried with dry benzene (3 x 2 mL) and placed under high vacuum for 4 h. The dry oil/gel was diluted in dry CH_2Cl_2 (0.1 M) and then bisdiisopropylamine cyanoethyl phosphoramidite (1.2–2.0 eq) was added to the reaction solution followed by the addition of tetrazole (0.45 M in CH_3CN, 1.0-2.0 eq). The reaction was monitored by TLC and allowed to stir at rt for 1 h before diluting with degassed CH_2Cl_2 (~10 mL). The organic phase was washed with degassed sat. $NaHCO_3$ and dried over $MgSO_4$. Once filtered and concentrated, the crude product was purified by gradient flash column chromatography (pre-treated with 3% TEA, 5 →20 % EtOAc:hexanes) to afford a mixture of diastereomers as a colorless oil: R_f = 0.50 (4:1 hexanes:EtOAc).

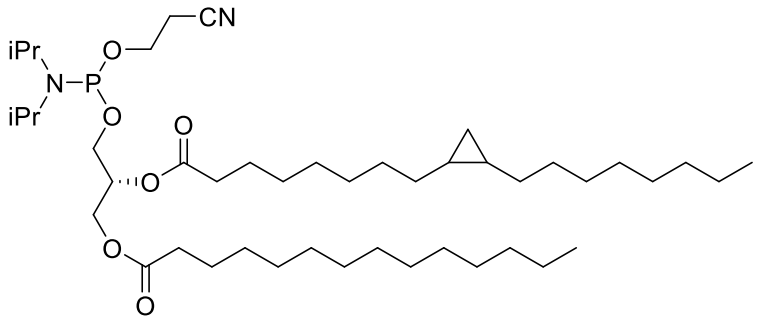


2-Cyanoethyl-*N,N*-diisopropylamine-(1,2-hexadecanoyl)-*sn*-glycero)-3-phosphoramidite (13): Diacylglyerol **5** (0.15 g, 0.30 mmol) was dissolved with dry CH_2Cl_2 (1.00 mL). Bisdiisopropylamine cyanoethyl phosphoramidite (0.19 mL, 0.59 mmol) was added followed by the addition of tetrazole (0.45 M in CH_3CN, 1.32 mL, 0.59 mmol). After 1 h at rt, the reaction was quenched and worked up as described in the general protocol. The crude mixture was purified by flash column chromatography to afford a mixture of diastereomers **13** (0.16 g, 77% yield) as a clear oil: R_f = 0.60 (4:1 hexanes:EtOAc); ^{1}H NMR (800 MHz, C_6D_6): δ 5.41 – 5.40 (m, *sn*-2-CH, 1H), 4.52 (dd, *J* = 11.9, 3.6 Hz, *sn*-1-CH_a, 0.5H), 4.44 (dd, *J* = 11.9, 3.6 Hz, *sn*-1-CH_a, 0.5H), 4.27 – 4.23 (m, *sn*-1-CH_b, 1H), 3.84 – 3.80 (m, *sn*-3-CH_2, 1H), 3.76 -3.68 (m, *sn*-3-CH_2, 1H), 3.52 – 3.49 (m, 2 x N-CH, 2H), 3.40 – 3.26 (m, PO-CH_2, 2H), 2.25 – 2.22 (m, CO-CH_2, 2H), 2.19 – 2.17 (m, CO-CH_2, 2H), 1.84 – 1.79 (m, NC-CH_2, 2H), 1.62 – 1.57 (m, 4H), 1.32 – 1.21 (m, 40H), 1.12 – 1.10 (m, 4 x $CHCH_3$, 12H), 0.91 (t, *J* = 7.1 Hz, 2 x CH_3, 6H); ^{13}C NMR (200 MHz, C_6D_6): δ 172.8, 172.6 (d, *J* = 3.6 Hz, *sn*-2-CO), 117.5 (d, *J* = 3.4 Hz, CN), 71.2 (app. t, *J* = 7.8, 7.8 Hz, *sn*-2-CH), 62.7 (d, *J* = 1.8 Hz, *sn*-1-CH_2), 62.2 (d, *J* = 15.9 Hz, *sn*-3-CH_2), 62.1 (d, *J* = 16.2 Hz, *sn*-3-CH_2), 58.9 (d, *J* = 18.4 Hz, PO-CH_2), 58.8 (d, *J* = 18.8 Hz, PO-CH_2), 43.5 (d, *J* = 4.7 Hz, N-CH), 43.4 (d, *J* = 4.7 Hz, N-CH), 34.5, 34.3, 32.4, 30.2, 30.2, 30.2, 30.1, 30.0, 29.9, 29.8, 29.7, 29.5, 25.3, 25.2, 24.7, 24.6, 23.1, 20.1 (d, *J* = 6.5 Hz, NC-CH_2), 14.4; ^{31}P NMR (200 MHz, $CDCl_3$): δ 149.7, 149.6; HRMS (ESI-Ion Trap) *m/z*: $[M+H]^+$ calcd for $C_{40}H_{78}N_2O_6P^+$, 713.5592; found 713.5578.



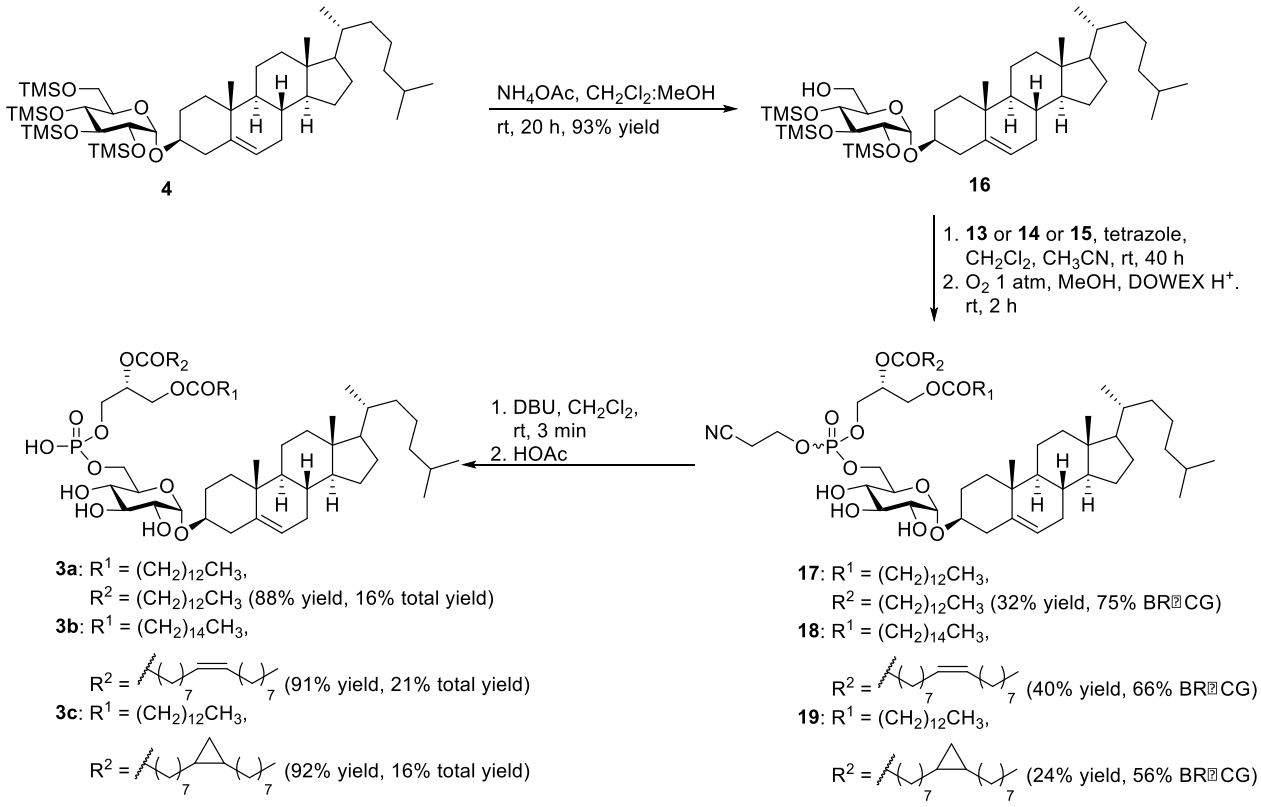
2-Cyanoethyl-*N,N*-diisopropylamine-(1-hexadecanoyl-2-(9Z-octadecanoyl)-*sn*-glycero)-3-phosphoramidite (14): 1-Palmitoyl-2-oleoyl-*sn*-glycerol **6** (0.12 g, 0.20 mmol) was dissolved in dry CH_2Cl_2 (1.8 mL) and then bisdiisopropylamine cyanoethyl phosphoramidite (0.08 mL, 0.24 mmol) was added to the reaction solution followed by the addition of tetrazole (0.45 M in CH_3CN, 0.44 mL, 0.20 mmol). The reaction stirred at rt for 1 h before diluting with degassed CH_2Cl_2 (~10 mL) and worked up as described in the general protocol. The crude product was purified by flash column chromatography to afford a mixture of diastereomers **14** as a colourless oil (0.13 g, 82% yield): R_f = 0.51 (4:1 hexanes:EtOAc); ^{1}H NMR (800 MHz, $CDCl_3$): δ 5.37 – 5.30 (m, HC=CH, 2H), 5.19 (m, *sn*-2-CH, 1H), 4.34 (ddd, *J* = 30.8, 11.9, 3.8 Hz, *sn*-3-CH_a, 1H), 4.16 (ddd, *J* = 22.2, 11.9, 6.3 Hz, *sn*-3-CH_b, 1H), 3.85 (m, CH_aCH_2CN, 1H), 3.82 – 3.75 (m, CH_bCH_2CN, *sn*-1-CH_a, 2H), 3.72 – 3.65 (m, *sn*-1-CH_b, 1H), 3.62 – 3.54 (m, 2xCH, 2H), 2.63 (m, CH_2CN, 2H), 2.33 – 2.27 (m, 4H), 2.00 (dt, *J* = 12.6, 6.5 Hz, 4H), 1.65 – 1.58 (m, 4H), 1.35 – 1.21 (m, 46H), 1.19 – 1.14 (m, 12H), 0.88 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (200 MHz, $CDCl_3$): δ 173.6, 173.1, 130.2 (C=C), 129.9 (C=C), 117.7 (C≡N), 70.8 (app. t, *J* = 7.4, 7.4 Hz, *sn*-2-C), 62.5 (d, *J* = 4.0 Hz, *sn*-1-C), 61.9 (d, *J* = 16.2 Hz, *sn*-3-C), 61.7 (d, *J* = 16.2 Hz, *sn*-3-C), 58.6 (app. t, *J* = 17.9, 17.9 Hz, CH_2CH_2CN), 43.3 (d, *J* = 2.9 Hz, N-CH), 43.2 (d, *J* = 2.9 Hz, N-CH), 34.45, 34.27, 32.07, 32.05, 29.91, 29.87, 29.85, 29.82, 29.81, 29.79, 29.67, 29.64, 29.51, 29.47, 29.45, 29.37, 29.36, 29.29, 29.24, 27.37, 27.32, 25.06, 25.04, 24.75, 24.71, 22.83, 20.5 (d, *J* =

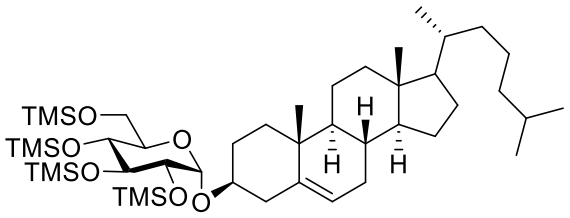
6.6 Hz, CH_2CN), 14.27, 1.16; ^{31}P NMR (200 MHz, $CDCl_3$): δ 149.5, 149.4; HRMS (ESI-Ion Trap) *m/z*: $[M+Na]^+$ calcd for $C_{46}H_{87}N_2O_6NaP$, 817.6199; found 817.6226.



2-Cyanoethyl-*N,N*-diisopropylamine-(1-hexadecanoyl-2-(9-cyclopropyl-nonadecanoyl)-*sn*-glycero)-3-phosphoramidite (15): Diacylglyerol **12** (0.14 g, 0.23 mmol) was dissolved with dry CH_2Cl_2 (1.00 mL). Bisdiisopropylamine cyanoethyl phosphoramidite (0.15 mL, 0.47 mmol) was added followed by the addition of tetrazole (0.45 M in CH_3CN, 1.03 mL, 0.47 mmol). After 1 h at room temperature, the reaction was quenched and worked up as described in the general protocol. The crude was purified by flash column chromatography to afford a mixture of diastereomers **15** (0.13 g, 82% yield) as a clear oil: $[\alpha]_D^{25}$ +3.11 (*c* 0.009, $CHCl_3$); R_f = 0.60 (4:1 hexanes:EtOAc); ^1H NMR (600 MHz, $CDCl_3$): δ 5.10 – 5.09 (m, *sn*-2-CH, 1H), 4.26 (dd, *J* = 11.9, 3.8 Hz, *sn*-1-CH_a, 0.5H), 4.22 (dd, *J* = 11.9, 3.8 Hz, *sn*-1-CH_a, 0.5H), 4.08 (dd, *J* = 11.9, 6.2 Hz, *sn*-1-CH_b, 0.5H), 4.05 (dd, *J* = 11.9, 6.2 Hz, *sn*-1-CH_b, 0.5H), 3.77 – 3.66 (m, *sn*-3-CH_{2a}, PO-CH_2, 3H), 3.62 – 3.58 (m, *sn*-3-CH_{2b}, 1H), 3.51 – 3.47 (m, 2x N-CH, 2H), 2.55 – 2.52 (m, NC-CH_2, 2H), 2.23 – 2.19 (m, 2xCO-CH_2, 4H), 1.52 – 1.49 (m, 4H), 1.27 – 1.15 (m, 44H), 1.08 (t, *J* = 6.7 Hz, 2x$CHCH_3$, 12H), 0.78 (t, *J* = 6.3 Hz, 2xCH_3, 6H), 0.56 – 0.52 (m, cyclopropyl 2xCH, 2H), 0.46 (ddd, *J* = 9.4, 4.1, 4.1 Hz, cyclopropyl CH_{2a}, 1H), -0.44 (app. q, *J* = 9.4, 5.3, 4.3 Hz, cyclopropyl CH_{2b}, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 173.5, 173.1 (d, *J* = 2.3 Hz, *sn*-2-CO), 117.7 (CN), 70.8 (d, *J* = 5.1 Hz, *sn*-2-CH), 70.7 (d, *J* = 5.1 Hz, *sn*-2-CH), 62.5 (d, *J* = 2.6 Hz, *sn*-1-CH_2), 61.9 (d, *J* = 16.4 Hz, *sn*-3-CH_2), 61.7 (d, *J* = 16.4 Hz, *sn*-3-CH_2), 58.7 (d, *J* =

12.4 Hz, PO-CH_2), 58.6 (d, J = 12.4 Hz, PO-CH_2), 43.4 (d, J = 1.9 Hz, N-CH), 43.3 (d, J = 1.9 Hz, N-CH), 34.5, 34.2, 32.1, 30.4, 30.3, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 28.9 28.8, 25.1, 25.0, 24.8, 24.7, 22.8, 20.5 (d, J = 6.7 Hz, NC-CH_2), 15.9 (cyclopropyl CH), 15.8 (cyclopropyl CH), 14.3, 11.1 (cyclopropyl CH_2); ^{31}P NMR (200 MHz, $CDCl_3$): δ 149.5, 149.4; HRMS (ESI-Ion Trap) *m/z*: $[M+H]^+$ calcd for $C_{45}H_{86}N_2O_6P^+$, 781.6218; found 781.6221.

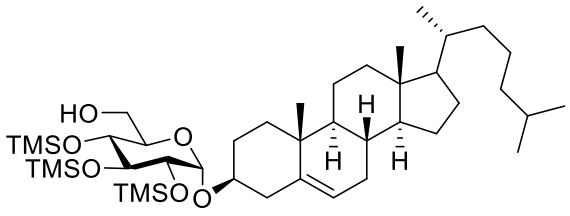




4

Cholesteryl 2,3,4,6-tetra-*O*-trimethylsilyl-α-D-glucopyranoside (4)[2] : In a flame dried argon purged round bottom containing 4 Å molecular sieves (300 mg) was added TBAI (140 mg, 0.38 mmol, 4.5 eq.), cholesterol (32 mg, 0.083 mmol, 1.0 eq.), and anhydrous dichloromethane (2.5 mL). Hünig's base (90 μL, 0.51 mmol, 6.0 eq.) was then added to the solution, which was stirred for 30 min. In a separate flame dried argon purged round bottom flask was placed per-*O*-trimethylsilylated glucose (140 mg, 0.25 mmol, 3.0 equiv). After azeotrope with anhydrous benzene (2 x 3 mL), per-*O*-TMS glucose was diluted with anhydrous dichloromethane (2.5 mL) and TMSI (40 μL, 0.28 mmol, 3.3 eq.) was added and allowed to react for 10 min at rt. The in situ generated glucosyl iodide was then transferred via cannula into the acceptor flask and allowed to stir for 2 d at rt. The solvent was then filtered to remove the molecular sieves and the solvent was removed under reduced pressure. A 1:1 ratio of ethyl acetate and hexanes (20 mL) was then added to the round bottom flask and the solution was cooled in a dry ice/acetone bath causing the excess TBAI to precipitate. The solid was filtered and the solution was again concentrated to give an oil. The crude mixture was purified by gradient flash column chromatography (0 →8 % hexanes:EtOAc) to afford **4** as a clear syrup (78 % yield): $[\alpha]_D^{25}$ +27.4 (*c* 0.002, $CHCl_3$); R_f = 0.29 (98:2 hexanes:EtOAc); ^{1}H NMR (600 MHz, C_6D_6): δ 5.41 (app. d, *J* = 5.1 Hz, H-6, 1H), 5.01 (d, *J* = 3.4 Hz, H-1', 1H), 4.20 (app. t, *J* = 8.9 Hz, 1H, H-3'), 3.96 (m, 1H, H-5'), 3.92 (dd, *J* = 3.7, 11.6 Hz, 1H, H-6'), 3.87 (app. t, *J* = 8.9 Hz, 1H, H-4'), 3.82 (dd, *J* = 1.5, 11.6 Hz, 1H, H-6''), 3.63 (dd, *J* = 3.4, 9.1 Hz, H-2', 1H), 3.61-3.57 (m, H-3, 1H), 2.57-2.47 (m, H-4, 2H), 2.00 (m, 1H), 1.94-1.89 (m, H-7, 2H), 1.84-1.81 (m, 1H), 1.71-1.69 (m, 1H), 1.61-

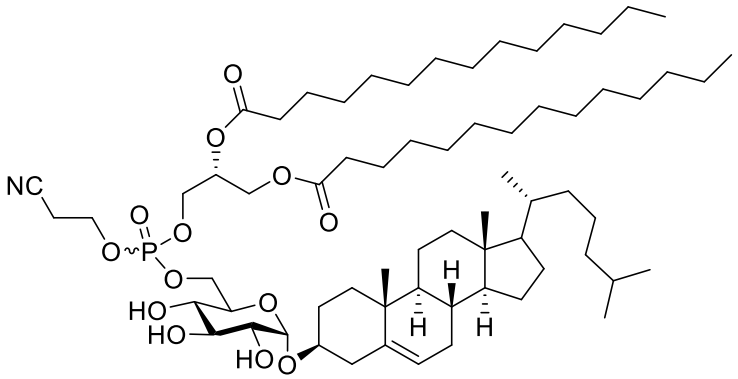
1.57 (m, H-2, 2H), 1.56-1.50 (m, 2H), 1.43-1.34 (m, 7H), 1.26-1.16 (m, 5H), 1.13-1.04 (m, 3H), 1.01-0.96 (m, 5H), 0.93 (dd, *J* = 1.8, 6.5 Hz, 7H), 0.88 (s, 3H), 0.65 (s, 3H), 0.33 (s, Si-$(CH_3)_3$, 9H), 0.31 (s, Si-$(CH_3)_3$, 9H), 0.19 (s, Si-$(CH_3)_3$, 9H), 0.13 (s, Si-$(CH_3)_3$, 9H); ^{13}C NMR (150 MHz, C_6D_6): δ 141.2 (C-5), 121.9 (C-6), 98.2 (C-1'), 78.0 (C-3), 75.5 (C-3'), 74.3 (C-2'), 73.3 (C-5'), 72.5 (C-4'), 62.3 (C-6'), 57.0, 56.5, 50.6, 42.6, 40.9, 40.2 (C-4), 40.0, 37.5, 37.0, 36.7, 36.2, 32.4 (C-7), 32.2, 28.7, 28.5, 28.4, 24.6, 24.4, 23.1, 22.8, 21.4, 19.5, 19.1, 12.1, 1.70, 1.24, 0.64, 0.01; HRMS (ESI-Ion Trap) *m/z*: $[M+Na]^+$ calcd for $C_{45}H_{88}O_6NaSi_4$, 859.5550; found 859.5578.



16

Cholesteryl 2,3,4-tri-*O*-trimethylsilyl-α-D-glucopyranoside (16): Glucoside **4** (0.14 g, 0.17 mmol) was azeotropically dried with dry benzene (3 x 3 mL) and placed under high vacuum for 6 h. To the clear foam was added NH_4OAc (0.03 g, 0.43 mmol) and the mixture was dissolved first with dry CH_2Cl_2 (1.00 mL) and then dry MeOH (1.00 mL) was added to the solution. The mixture was then stirred at rt for 16 h and then concentrated for gradient flash column chromatography (pre-treated with 4 % TEA in hexanes, 0 →10 % EtOAc:hexanes) to afford **16** as a clear foam (0.12 g, 93% yield): $[\alpha]_D^{25}$ +20.0 (*c* 0.002, $CHCl_3$); R_f= 0.32 (92:8 hexanes:EtOAc); ^{1}H NMR (600 MHz, C_6D_6): δ 5.40 (app. d, *J* = 4.0 Hz, H-6, 1H), 4.98 (d, *J* = 3.5 Hz, H-1', 1H), 4.20 (app. t, *J* = 8.9 Hz, H-3', 1H), 3.99 (m, H-5', 1H), 3.87 – 3.72 (m, H-4', H-6', H-6'', 3H), 3.59 (dd, *J* = 9.2, 3.6 Hz, H-2', 1H), 3.57 – 3.53 (m, H-3, 1H), 2.51 (d, *J* = 7.6

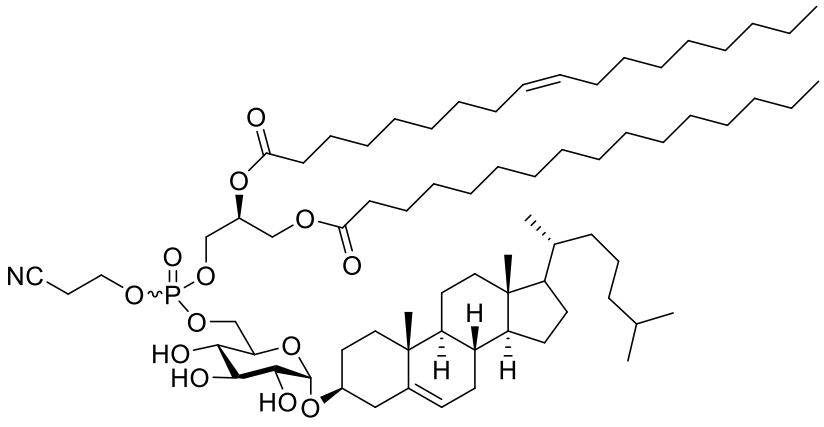
Hz, H-4, 2H), 2.03 (m, 1H), 1.98 – 1.89 (m, H-7, 2H), 1.89 – 1.81 (m, 1H), 1.74 (m, 1H), 1.67 – 1.59 (m, 2H), 1.55 (m, 3H), 1.48 – 1.17 (m, 14H), 1.16 – 1.05 (m, 3H), 1.02 (d, J = 6.5 Hz, 4H), 0.94 (dd, J = 6.6, 1.5 Hz, 8H), 0.90 – 0.86 (m, 3H), 0.67 (s, 3H), 0.33 (s, 9H), 0.31 (s, 9H), 0.19 (s, 9H); ^{13}C NMR (150 MHz, C_6D_6): δ 141.0 (C-5), 122.1 (C-6), 98.3 (C-1'), 78.3 (C-3), 75.1 (C-3'), 74.2 (C-2'), 73.0 (C-5'), 72.4 (C-4'), 61.9 (C-6'), 57.0, 56.6, 54.4, 50.6, 46.5, 42.6, 42.1, 40.8, 40.2, 40.0, 37.6, 37.1, 37.0, 36.7, 36.2, 32.4, 32.2, 30.2, 28.7, 28.5, 28.5, 24.6, 24.4, 23.1, 22.8, 21.4, 19.4, 19.1, 12.1, 1.61, 1.14, 0.63; HRMS (ESI-Ion Trap) *m/z*: $[M+Na]^+$ calcd for $C_{42}H_{80}O_6NaSi_3$, 787.5160; found 787.5145.



17

Cholesteryl 6-*O*-(1,2-tetradecanoyl-*sn*-glycero-3-phosphocyanoethyl)-α-D-glucopyranoside (17): Glucoside **16** (0.04 g, 0.06 mmol) and phosphoramidite **13** (0.16 g, 0.23 mmol) were azeotropically dried with dry benzene (3 x 5 mL) and placed under high vacuum for 15 h. The mixture was then diluted in dry CH_2Cl_2 (0.50 mL) and tetrazole (0.45 M in CH_3CN, 0.82 mL) was added. After stirring at rt for 40 h, the reaction mixture was diluted with CH_2Cl_2 (2 mL) and O_2 gas was bubbled through the mixture for 30 min. DOWEX H^+ (0.20 g) was added to the reaction and left stirring under O_2 for an additional 4 h. The DOWEX H^+ was filtered and washed with $CHCl_3$. The filtrate was then washed with sat. $NaHCO_3$, dried over $MgSO_4$, filtered, and concentrated for gradient flash column chromatography (0 →10% MeOH:EtOAc

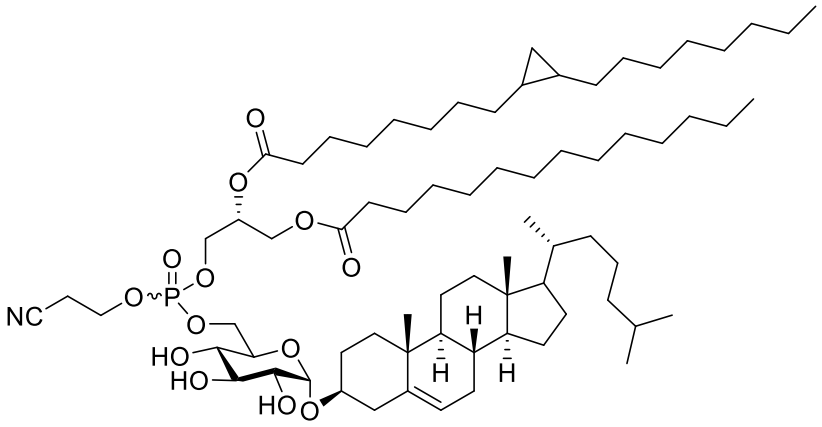
and then flushed with 30% MeOH:EtOAc) to afford a mixture of diastereomers of **17** (0.02 g, 32% yield, 75% BRSM): R_f = 0.58 (9:1 EtOAc: MeOH); ^{1}H NMR (600 MHz, $CDCl_3$:MeOD 5:1) δ 5.29 – 5.28 (m, H-6, 1H), 5.23 – 5.17 (m, *sn*-2-CH, 1H), 4.92 (d, *J* = 3.6 Hz, H-1', 1H), 4.31 – 4.09 (m, *sn*-1-CH_2, *sn*-3-CH_2, PO-CH_2, H-6', 8H), 3.78 – 3.74 (m, H-5', 1H), 3.60 (app. t, *J* = 8.9, 8.9 Hz, H-3', 1H), 3.42 – 3.38 (m, H-3, 1H), 3.36 (dd, *J* = 8.9, 3.6 Hz, H-2', 1H), 3.34 – 3.32 (m, H-4', 1H), 2.76 – 2.74 (m, NC-CH_2, 2H), 2.30 – 2.25 (m, 2xCO-CH_2, H-4, 6H), 1.97 – 1.90 (m, H-7, 2H), 1.87 – 1.74 (m, 3H), 1.57 – 1.53 (m, 5H), 1.49 – 1.37 (m, 6H), 1.27 – 1.17 (m, 45H), 1.12 – 0.98 (m, 7H), 0.95 (s, 3H), 0.93 – 0.89 (m, 2H), 0.86 – 0.79 (m, 15H), 0.62 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$:MeOD 5:1) δ 173.6, 173.5, 173.2, 173.1, 140.5 (C-5), 122.0 (C-6), 121.9 (C-6), 116.5 (CN), 116.4 (CN), 97.1 (C-1'), 97.0 (C-1'), 78.2 (C-3), 78.1 (C-3), 73.9 (C-3'), 73.8 (C-3'), 71.8 (C-2'), 70.3 (C-5'), 70.2 (C-5'), 69.3 (app. t, *J* = 7.5, 7.5 Hz, *sn*-2-CH, C-4'), 67.5 (d, *J* = 5.4 Hz, C-6'), 67.4 (d, *J* = 5.4 Hz, C-6'), 66.0 (app. t, *J* = 5.0, 5.0 Hz, *sn*-3-CH_2), 62.4 (d, *J* = 5.7 Hz, PO-CH_2), 62.3 (d, *J* = 5.2 Hz, PO-CH_2), 61.7 (*sn*-1-CH_2), 61.6 (*sn*-1-CH_2), 56.7, 56.1, 50.1, 42.2, 40.0, 39.7, 39.4, 36.9, 36.6, 36.1, 35.7, 34.1, 33.9, 31.8, 31.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 28.1, 27.9, 27.7, 24.8, 24.2, 23.7, 22.6, 22.5, 22.4, 20.9, 19.4, 19.3, 19.2, 18.6, 13.9, 11.7; ^{31}P NMR (200 MHz, $CDCl_3$:MeOD 5:1): δ -1.62; HRMS (ESI-Ion Trap) *m/z*: $[M+NH_4]^+$ calcd for $C_{67}H_{122}N_2O_{13}P^+$, 1193.8679; found 1193.8807.



18

Cholesteryl 6-*O*-(1-hexadecanoyl-2-(9*Z*-octadecanoyl)-*sn*-glycero-3-phosphocyanoethyl)-α-D-glucopyranoside (18): Glucoside **16** (0.03 g, 0.03 mmol) and phosphoramidite **14** (0.11 g, 0.14 mmol) were azeotropically dried with dry benzene (3 x 5 mL) and placed under high vacuum for 2 h. The mixture was then diluted in dry CH_2Cl_2 (0.5 mL) and tetrazole (0.45 M in CH_3CN, 0.47 mL) was added. After stirring at rt for 40 h, the reaction mixture was diluted with CH_2Cl_2 (2 mL) and O_2 gas was bubbled through the mixture for 30 min. DOWEX H^+ (0.20 g) was added to the reaction and left stirring under O_2 for an additional 4 h. The DOWEX H^+ was filtered and washed with $CHCl_3$. The filtrate was then washed with sat. $NaHCO_3$, dried over $MgSO_4$, filtered, and concentrated for gradient flash column chromatography (0 →10% MeOH:EtOAc and then flushed with 30% MeOH:EtOAc) to afford a mixture of diastereomers of **18** (0.02 g, 40% yield, 66% BRSM): R_f = 0.58 (9:1 EtOAc: MeOH); ^{1}H NMR (600 MHz, $CDCl_3$:MeOD 5:1) δ 5.40 – 5.29 (m, 3H, HC=CH, H-6), 5.26 (m, 1H, *sn*-2-CH), 5.03 (d, *J* = 3.7 Hz, 1H, H-1'), 4.45 (m, 1H, H-6'), 4.38 – 4.13 (m, 7H, *sn*-1-CH_2, *sn*-3-CH_2, CH_2CH_2CN, H-6''), 3.86 – 3.77 (m, 1H, H-5'), 3.73 (m, 1H, H-3'), 3.59 – 3.52 (m, 1H, H-4'), 3.52 (m, 2H, H-2', H-3), 2.78 (m, 2H, CH_2CN), 2.34 (m, 6H, 2xCO-CH_2, H-4), 2.01 (m, 6H, CH_2CH=$CHCH_2$, H-7), 1.88 (m, 4H), 1.61 (m, 6H), 1.54 – 1.40 (m, 6H), 1.38 – 1.19 (m, 45H), 1.18 – 1.04 (m, 8H), 1.04

– 0.95 (m, 6H), 0.88 (m, 17H), 0.68 (s, 3H); ^{1}H NMR (600 MHz, C_5D_5N:MeOD) δ 5.79 – 5.73 (m, 1H, *sn*-2-CH), 5.59 (bs, 1H, H-6), 5.57 – 5.50 (m, 3H, HC=CH, H-1'), 4.96 – 4.86 (m, 2H, H-6', H-6''), 4.81 – 4.70 (m, 2H, H-4', *sn*-1-CH_a), 4.61 (m, 6H, *sn*-1-CH_b, *sn*-3-CH_2, CH_2CH_2CN, H-3'), 4.15 (dd, *J* = 3.7, 9.6 Hz, 1H, H-2'), 4.13 – 4.08 (m, 1H, H-5'), 3.89 – 3.78 (m, 2H, H-3), 3.16 – 3.07 (ddd, *J* = 6.2, 6.2, 18.7 Hz, 2H, CH_2CN), 2.80 – 2.71 (m, 1H, H-4), 2.63 – 2.47 (m, 4H, 2xCO-CH_2), 2.17 (m, 4H, CH_2CH=$CHCH_2$), 2.06 (m, 2H, H-7), 1.95 – 1.81 (m, 3H), 1.74 (m, 4H), 1.71 – 1.62 (m, 3H), 1.58 (m, 2H), 1.50 – 1.40 (m, 8H), 1.40 – 1.25 (m, 34H), 1.24 – 1.17 (m, 4H), 1.17 – 1.09 (m, 3H), 1.07 – 0.99 (m, 6H), 0.98 – 0.87 (m, 11H), 0.74 (m, 3H); ^{13}C NMR (150 MHz, C_5D_5N:MeOD) δ 173.6, 173.4, 141.6 (C-5), 130.7 (HC=CH), 130.6 (HC=CH), 122.4 (C-6), 118.3 (C≡N), 99.46 (C-1'), 99.43 (C-1'), 80.3 (C-3), 78.7, 77.8 (CH_2CH_2CN), 75.9 (C-2'), 74.4 (C-3'), 72.8 (C-5'), 72.7 (C-5'), 72.1 (C-4'), 71.9 (d, *J* = 6.2 Hz, *sn*-2-CH), 69.3 (d, *J* = 6.8 Hz, C-6'), 66.8 (d, *J* = 3.7 Hz, *sn*-3-C), 63.4, 62.7 (*sn*-1-C), 57.2, 56.8, 56.7, 50.7, 42.9, 41.1, 40.4, 40.2, 37.8, 37.3, 36.9, 36.5, 34.8, 34.6, 32.7, 32.5, 32.5, 30.5, 30.4, 30.4, 30.4, 30.4, 30.3, 30.2, 30.1, 30.1, 30.0, 30.0, 29.9, 29.8, 29.8, 28.9, 28.8, 28.8, 28.7, 28.0, 25.6, 24.9, 24.6, 23.4, 23.3, 23.1, 21.7, 20.3, 20.2, 19.9, 19.4, 14.7, 12.4; ^{31}P NMR (200 MHz, $CDCl_3$): δ -0.52, -0.56; HRMS (ESI-Ion Trap) *m/z*: $[M+NH_4]^+$ calcd for $C_{73}H_{132}N_2O_{13}P^+$, 1275.9462; found 1275.9510.

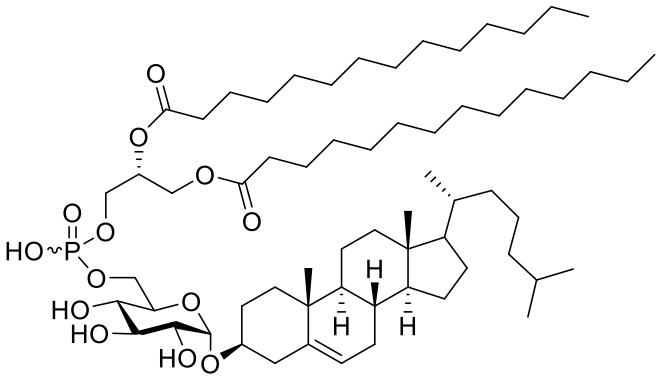


19

Cholesteryl 6-*O*-(1-tetradecanoyl-2-(9-cyclopropyl-nonadecanoyl)-*sn*-glycero-3-phosphocyanoethyl)-α-D-glucopyranoside (19): Glucoside **16** (0.05 g, 0.06 mmol) and phosphoramidite **15** (19 g, 0.25 mmol) were azeotropically dried with dry benzene (3 x 5 mL) and placed under high vacuum for 16 h. The mixture was then diluted in dry CH_2Cl_2 (0.50 mL) and tetrazole (0.45 M in CH_3CN, 0.89 mL, 0.40 mmol) was added. After stirring at rt for 40 h, the reaction mixture was diluted with CH_2Cl_2 (2 mL) and O_2 gas was bubbled through the mixture for 30 min. DOWEX H^+ (0.25 g) was added to the reaction and left stirring under O_2 for an additional 4 h. The DOWEX H^+ was filtered and washed with $CHCl_3$. The filtrate was then washed with sat. $NaHCO_3$, dried over $MgSO_4$, filtered, and concentrated for gradient flash column chromatography (0 →10% MeOH:EtOAc and then flushed with 30% MeOH:EtOAc) to afford a mixture of diastereomers of **19** (0.02 g, 24% yield, 56% BRSM): R_f = 0.58 (9:1 EtOAc: MeOH); ^{1}H NMR (800 MHz, $CDCl_3$:MeOD 1:1) δ 5.35 – 5.32 (m, H-6, 1H), 5.28 – 5.24 (m, *sn*-2-CH, 1H), 4.95 (d, *J* = 3.5 Hz, H-1', 1H), 4.38 – 4.34 (m, *sn*-1-CH_{2a}, 1H), 4.33 – 4.30 (m, H-6', 2H), 4.29 – 4.19 (m, PO-CH_2, *sn*-3-CH_{2a}, 3H), 4.18 – 4.14 (m, *sn*-1-CH_{2b}, *sn*-3-CH_{2b}, 2H), 3.84 – 3.76 (m, H-5', 1H), 3.78 – 3.62 (m, H-3', 1H), 3.49 – 3.41 (m, H-3, 1H), 3.38 (dd, *J* = 9.6, 3.6 Hz, H-2', 1H), 3.34 – 3.30 (m, H-4', 1H), 3.16 (TEA), 2.85 – 2.82 (m, NC-CH_2, 2H), 2.36 – 2.30 (m, 2xCO-CH_2, H-4, 5H), 2.01- 1.98 (m, H-7, 2H), 1.97 – 1.79 (m, 3H), 1.63 – 1.56 (m, 5H),

1.53 -1.40 (m, 5H), 1.39 – 1.18 (m, 55H), 1.18 – 1.02 (m, 8H), 1.00 (s, 3H), 0.93 – 0.81 (m, 15H), 0.67 (s, 3H), 0.65 – 0.61 (m, cyclopropyl 2xCH, 2H), 0.54 (ddd, J = 8.2, 3.9, 4.2 Hz, cyclopropyl CH_{2a}, 1H), -0.36 (app. q, J = 8.2, 4.8, 4.8 Hz, cyclopropyl CH_{2b}, 1H); ^{13}C NMR (200 MHz, $CDCl_3$:MeOD 1:1) δ 174.3, 173.8, 141.3 (C-5), 141.2 (C-5), 122.5 (C-6), 122.4 (C-6), 117.4 (CN), 117.3 (CN), 97.9 (C-1'), 97.9 (C-1'), 78.9 (C-3), 78.8 (C-3), 74.4 (C-3'), 72.5 (C-2'), 71.1 (C-5'), 71.0 (C-5'), 70.4 (C-4'), 70.3 (C-4'), 70.1 (*sn*-2-CH), 70.0 (*sn*-2-CH), 68.5 (d, J = 5.3 Hz, C-6'), 68.3 (d, J = 3.5 Hz, C-6'), 66.8 (d, J = 5.5 Hz, *sn*-3-CH_2), 66.7 (d, J = 5.0 Hz, *sn*-3-CH_2), 63.2 (d, J = 5.2 Hz, PO-CH_2), 63.1 (d, J = 4.7 Hz, PO-CH_2), 62.4 (*sn*-1-CH_2), 62.3 (*sn*-1-CH_2), 57.4, 56.8, 50.8, 47.3, 42.9, 40.7, 40.4, 40.1, 37.6, 37.3, 36.7, 36.4, 34.7, 34.5, 34.5, 32.5, 30.7, 30.2, 30.2, 30.1, 30.0, 29.9, 29.9, 29.8, 29.7, 29.7, 29.6, 29.3, 29.2, 28.8, 28.5, 28.3, 25.4, 25.4, 24.8, 24.3, 23.2, 23.1, 22.8, 21.6, 19.9, 19.7, 19.1, 16.3, 16.2, 14.3, 12.2, 11.3, 9.1 (cyclopropyl CH_2); ^{31}P NMR (200 MHz, $CDCl_3$:MeOD 1:1): δ -1.94; HRMS (ESI-Ion Trap) *m/z*: $[M+NH_4]^+$ calcd for $C_{72}H_{130}N_2O_{13}P^+$, 1261.9305; found 1261.9305.

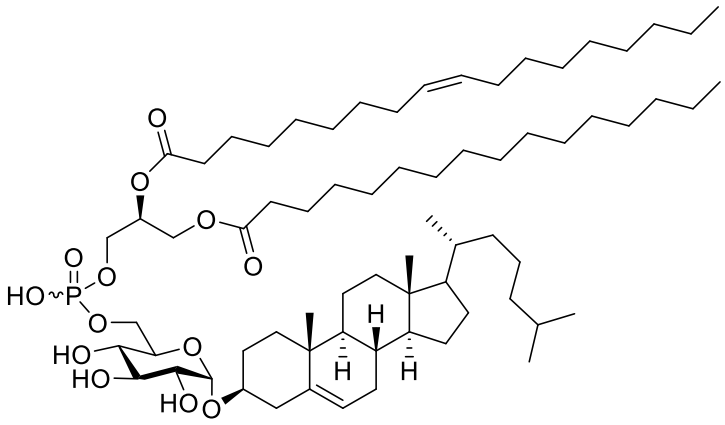
General protocol for the deprotection of 17-19: Compound (**17-19**) was dissolved with dry CH_2Cl_2 (1.00 mL) and DBU (20 μL). The reaction was stirred at rt for 3 min and then quenched with HOAc (20 μL). Progress of the reaction was followed by TLC (R_f of αCPG 0.56-0.7 using 7:3:0.5 $CHCl_3$:MeOH:NH_4OH 0.1 M and the spot is below the spot for αCG) The solution was then concentrated and purified gradient flash column chromatography (5:4:1 $CHCl_3$:Acetone:IPA →5:4:1 $CHCl_3$:Acetone:MeOH →5:3:2 $CHCl_3$:Acetone:MeOH) to afford αCPG (**3a-3c**).



3a

Cholesteryl 6-*O*-(1,2-hexadecanoyl-*sn*-glycero-3-phosphate)-α-D-glucopyranoside (3a): Glucoside **18** (6 mg, 0.1 mmol) was dissolved in dry CH_2Cl_2 (1.0 mL) and deprotected according to the general procedure above. After work-up and purification αCPG **3a** (5 mg, 88% yield) was attained as an amorphous white solid: $[\alpha]_D^{24}$ +24.0 (*c* 0.001, $CHCl_3$:MeOH 1:1); R_f = 0.60 (7:3:0.5 $CHCl_3$:MeOH:NH_4OH 0.1 M); ^{1}H NMR (600 MHz, $CDCl_3$:MeOD:TEA 0.1M in $CDCl_3$ 4:1.5:0.5): δ 5.30 (app. br. s, H-6, 1H), 5.19 (app. br. s, *sn*-2-CH, 1H), 4.93 (app. br. s, H-1', 1H), 4.37 – 4.35 (m, *sn*-1-CH_{2a}, 1H), 4.21 – 4.10 (m, *sn*-1-CH_{2b}, H-6', 2H), 3.95 (app. br. s, *sn*-3-CH_2, 2H), 3.91 – 3.85 (m, H-6", 1H), 3.69 – 3.58 (m, H-5', H-3', 2H), 3.57 – 3.49 (m, H-4', 1H), 3.46 – 3.36 (m, H-3, H-2', 2H), 2.68 (TEA), 2.29 – 2.25 (m, H-4, 2xCO-CH_2, 6H), 2.03 – 1.74 (m, H-7, 5H), 1.62 – 1.38 (m, 10H), 1.36 – 1.16 (m, 37H), 1.08 (TEA), 0.96 (s, 4H), 0.91 – 0.78 (m, 12H), 0.64 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$:MeOD:TEA 0.1M in $CDCl_3$ 4:1.5:0.5): δ 174.2, 173.8, 140.7 (C-5), 122.3 (C-6), 97.4 (C-1'), 78.2 (C-3), 73.4 (C-3'), 72.4 (C-2'), 71.6 (d, *J* = 3.2 Hz, C-5'), 70.7 (d, *J* = 8.3 Hz, *sn*-2-CH), 69.2 (C-4'), 64.4 (d, *J* = 5.6 Hz, C-6'), 63.9 (d, *J* = 4.6 Hz, *sn*-3-CH_2), 62.8 (*sn*-1-CH_2), 57.0, 56.4, 50.4, 46.1 (TEA), 42.6, 40.3, 40.0, 39.8, 37.3, 36.9, 36.4, 36.1, 34.5, 34.3, 32.2, 29.9, 29.9, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 28.5, 28.2, 27.9, 25.2, 25.1, 24.5, 24.1, 22.9, 22.7, 21.3, 19.5, 18.9, 14.2, 12.0 10.1 (TEA); ^{31}P NMR (200 MHz,

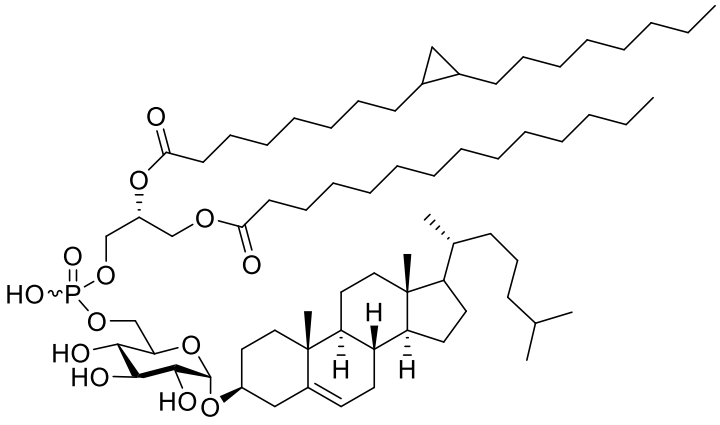
$CDCl_3$:MeOD:TEA 0.1M in $CDCl_3$ 4:1.5:0.5): δ 1.41 ; HRMS (ESI-Ion Trap) *m/z*: $[M-1]^-$ calcd for $C_{64}H_{114}O_{13}P^-$, 1121.8003; found 1121.7961.



3b

Cholesteryl 6-*O*-(1-hexadecanoyl-2-(9Z-octadecanoyl)-*sn*-glycero-3-phosphate)-α-D-glucopyranoside (3b): Compound **20** (0.02 g, 0.02 mmol) was diluted in CH_2Cl_2 (1.00 mL) and then DBU (0.02 mL, 0.13 mmol) was added to the solution. The reaction was stirred for 3 min before being quenched with HOAc (0.02 mL). The crude mixture was then concentrated for gradient flash column chromatography (9:1 EtOAc:MeOH → 60:20:1 $CHCl_3$:MeOH:H_2O) to afford **3b** as a gel (17 mg, 91% yield): $[\alpha]_D^{25}$ +36.8 (*c* 0.001, $CHCl_3$:MeOH 4:1); R_f = 0.56 (7:3:0.5 $CHCl_3$:MeOH:NH_4OH 0.1 M); ^{1}H NMR (800 MHz, $CDCl_3$:DBU:CD_3COOD): δ 5.38 – 5.28 (m, HC=CH, H-6, 3H), 5.22 (m, *sn*-2-CH, 1H), 5.01 (d, *J* = 3.5 Hz, H-1', 1H), 4.42 (app. t, *J* = 11.7 Hz, H-6', 1H), 4.38 (dd, *J* = 2.3, 11.8 Hz, *sn*-1-CH_a, 1H), 4.17 (dd, *J* = 11.9, 6.5 Hz, *sn*-1-CH_b, 1H), 4.00 (m, *sn*-3-CH_2, 2H), 3.94 – 3.86 (m, H-6" , 1H), 3.80 (app. t, *J* = 9.4 Hz, H-3', 1H), 3.67 – 3.58 (m, H-4', H-5', 2H), 3.48 (m, DBU, H-2', H-3, 21H), 2.30 (m, 2xCO-CH_2, H-4, 6H), 2.05 – 1.93 (m, DBU, CH_2CH=CH-CH_2, H-7, 17H), 1.85 – 1.71 (m, DBU, 17H), 1.72 – 1.61 (m, 13H), 1.61 – 1.54 (m, 6H), 1.54 – 1.39 (m, 8H), 1.40 – 1.18 (m, 58H), 1.18 – 1.03 (m, 10H), 1.00 (m, 6H), 0.94 – 0.76 (m, 22H), 0.69 (s, 3H); ^{13}C NMR (200 MHz,

$CDCl_3$:DBU:CD_3COOD): δ 173.6, 173.2, 140.6 (C-5), 130.2 (C=C), 129.9 (C=C), 122.2 (C-6), 97.2 (C-1'), 78.0 (C-3), 73.9 (C-3'), 72.7 (C-2'), 72.1 (d, *J* = 2.6 Hz, C-5'), 70.6 (d, *J* = 4.3 Hz, *sn*-2-CH), 68.9 (C-4'), 64.2 (d, *J* = 6.8 Hz, C-6'), 63.7 (d, *J* = 4.3 Hz, *sn*-3-CH_2), 62.8 (*sn*-1-CH_2), 56.9, 56.3, 50.2, 49.7, 45.1, 42.4, 40.2, 39.9, 39.7, 37.3, 37.1, 36.8, 36.3, 35.9, 35.3, 34.5, 34.3, 32.4, 32.1, 32.0, 30.1, 29.9, 29.8, 29.7, 29.5, 29.4, 28.6, 28.4, 28.2, 27.4, 27.3, 25.1, 24.5, 24.0, 23.6, 23.0, 22.9, 22.7, 21.2, 19.5, 18.9, 14.3, 12.0; ; ^{31}P NMR (200 MHz, $CDCl_3$): δ 2.41 ; HRMS (ESI-Ion Trap) *m/z*: $[M-1]^-$ calcd for $C_{70}H_{124}O_{13}P^-$, 1203.8785; found 1203.8781.



3c

Cholesteryl 6-*O*-(1-tetradecanoyl-2-(9-cyclopropyl-nonadecanoyl)-*sn*-glycero-3-phosphate)-α-D-glucopyranoside (3c): Glucoside **20** (0.02 g, 0.1 mmol) was dissolved in dry CH_2Cl_2 (1.0 mL) and deprotected according to the general procedure above. After work-up and purification αCPG **3c** (14 mg, 92% yield) was attained as an amorphous chalk white solid: $[\alpha]_D^{24}$ +16.3 (*c* 0.001, $CHCl_3$:MeOH 4:1); R_f = 0.61 (7:3:0.5 $CHCl_3$:MeOH:NH_4OH 0.1 M); ^1H NMR (800 MHz, $CDCl_3$:MeOD 1:1): δ 5.33 (app. br. s, H-6, 1H), 5.22 (app. br. s, *sn*-2-CH, 1H), 4.94 (app. br. s, H-1', 1H), 4.42 – 4.41 (m, *sn*-1-CH_{2a}, 1H), 4.20 – 4.14 (m, *sn*-1-CH_{2b}, H-6'a, 2H), 3.99 – 3.92 (m, *sn*-3-CH_2, H-6'b, 3H), 3.68 – 3.60 (m, H-5', H-3', 2H), 3.57 – 3.49 (m, H-4', 1H), 3.47

– 3.37 (m, H-3, H-2', 2H), 2.33 – 2.27 (m, 2xCO-CH_2, H-4, 6H), 2.01 – 1.99 (m, H-7, 1H), 1.96 -1.94 (m, 2H), 1.86 – 1.82 (m, 3H), 1.58 – 1.57 (m, 6H), 1.51 – 1.41 (m, 7H), 1.36 – 1.18 (m, 56H), 1.17 – 1.03 (m, 11H), 1.01 – 0.94 (m, 6H), 0.92 – 0.83 (m, 22H), 0.67 (s, 3H), 0.65 – 0.61 (m, cyclopropyl 2x CH, 2H), 0.55 (ddd, J = 9.4, 4.2, 3.9 Hz, cyclopropyl CH_{2a}, 1H), -0.36 (app. q, J = 9.4, 4.9, 4.9 Hz, cyclopropyl CH_{2b}, 1H); ^{13}C NMR (200 MHz, $CDCl_3$:MeOD 1:1): δ 174.5, 174.2, 141.2 (C-5), 122.5 (C-6), 97.9 (C-1'), 78.5 (C-3), 73.9 (C-3'), 72.8 (C-2'), 71.9 (d, J = 5.3 Hz, C-5'), 71.1 (d, J = 6.4 Hz, *sn*-2-CH), 69.9 (C-4'), 64.9 (d, J = 6.4 Hz, C-6'), 64.3 (d, J = 4.3 Hz, *sn*-3-CH_2), 63.2 (*sn*-1-CH_2), 57.4, 56.8, 50.8, 49.5, 49.4, 42.9, 40.7, 40.4, 40.1, 37.7, 37.3, 36.8, 36.4, 34.8, 34.6, 32.5, 30.8, 30.7, 30.3, 30.3, 30.2, 30.2, 30.2, 30.1, 30.1, 30.1, 30.0, 29.9, 29.9, 29.8, 29.7, 29.3, 28.8, 28.5, 28.2, 25.5, 25.4, 24.8, 24.4, 23.2, 23.1, 22.8, 21.6, 19.7, 19.1, 16.3 (cyclopropyl CH), 16.2 (cyclopropyl CH), 14.4, 12.2, 11.3 (cyclopropyl CH_2); ^{31}P NMR (200 MHz, $CDCl_3$:MeOD 1:1): δ 0.83 ; HRMS (ESI-Ion Trap) *m/z*: $[M-1]^-$ calcd for $C_{69}H_{122}O_{13}P^-$, 1189.8629; found 1189.8588.

References

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